REVIEW

The k$_0$-IAEA program*

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New software was developed to assist users of the k$_0$-approach in NAA to harmonize their results. The k$_0$-IAEA software uses the holistic approach developed at the Delft Interfaculty Reactor Institute and incorporates the latest k$_0$ data catalogue together with additional information on coincidence and sum peaks, which together are used in the joint evaluation of samples. Multiple irradiations as well as multiple measurements of samples are treated simultaneously. Flux parameter determination as well as efficiency calibrations of detectors are accommodated using a single-measurement approach as developed at the Interfaculty Reactor Institute, Delft. The standard Windows software will stimulate the application of the k$_0$ approach through the free distribution and updates of the program.

Introduction

In recent years the International Atomic Energy Agency (IAEA) has helped many institutes in developing Member States set up nuclear analytical laboratories through assistance via technical co-operation and coordinated research projects, expert services, and fellowship awards. Some of these laboratories have by now established good laboratory practice or quality systems and are providing service analysis to customers in many fields, including geological prospecting, environmental contamination survey or biomedical investigations. Neutron activation analysis (NAA), being the workhorse in nuclear analytical laboratories whenever an intense neutron source for irradiation of samples is available, is a non-destructive, multi-element determination method with a high degree of accuracy and reliability. Automation of the counting and data evaluation process to increase sample throughput and standardizing the procedure is a great challenge at many INAA laboratories. In the recent past k$_0$ software was developed at various NAA laboratories using different approaches. This method is now well established in the nuclear analytical community. Although the data catalogue for use in k$_0$ calculation is under constant refinement the basic routines for the k$_0$ evaluation of element contents in samples are in place and need to be linked appropriately. A commercial software package for this purpose is available; however, it is too costly for many of the research laboratories. A program with a standard Windows user interface, incorporating newly developed features, was developed to be distributed free of charge by the IAEA, in order to further encourage NAA laboratories to rely on k$_0$-standardization rather than on synthetic standard calibration and evaluation. This software package should strongly promote the harmonization of analytical results from NAA laboratories by eliminating bias related to the computation of results, as well as to standard preparation difficulties. The method-validation material SMELS[1] as well as suitable materials for irradiation facility characterization will be associated with the software distribution. Introducing the k$_0$ software and making it available free of charge would hopefully diminish abuse of certified reference materials for calibration purposes.

A consistently used program for calculation of results based on a well-determined set of physical constants will inevitably improve the harmonization of analytical results and strengthen the nuclear community versus their non-nuclear competitors.

It is foreseen in the near future to incorporate additional modules in the k$_0$-IAEA software, such as peak area determination to make data input less cumbersome, and the implementation of PGNAA. As a new updated catalogue for k$_0$ values for prompt reactions is now available[10] the growing PGNAA community will appreciate the option to use the same software for prompt and delayed gamma-spectra for simultaneous interpretation of such spectra even. This new software, due to the universal holistic approach, can accommodate such diverse applications and will be made available in due time for a larger community of users of nuclear analytical techniques.

Description of the program

Nuclear data

In most parts of the program, nuclear data are required. The primary database used was the k_0-database,[2] as accessible at the k_0 website,[3] supplemented with the database in use at the Interfaculty Reactor Institute in Delft. A somewhat outdated version of this last, combined database has been published as well.[4] Also needed are the decay schemes of the radionuclides. These were taken from the Table of Isotopes.[5]

Coincidence summing

The algorithm performing these calculations in the program takes all known phenomena into account, such as photo peaks, escape and double escape peaks, as well as coincidence summing between gamma-rays, or involving X-rays following electron capture or internal conversion. The exceptions are angular correlations, coincidence losses due to Bremsstrahlung and finally, no measures are taken to correct for extended sources measured close to the end cap.

Detector calibration

A mixture of methods is incorporated in the k_0-IAEA program, composed of a proposed approach by DE FELICE et al.,[6] where one measurement of, e.g., ^{137}Cs would be employed to determine the peak-to-total curve in its entirety, and of the Delft approach[7] which is used for the efficiency curve fit, knowing the peak-to-total and taking coincidence summing into account. This procedure was expected to be stable and applicable to most counting geometries used in INAA, even to and small sources close to the end cap well-type detectors.

Upon further investigation, it appeared that DE FELICE's method sets the peak-to-total ratio equal to unity for all energies below 160 keV, so the (160 keV, 1) data point is a given, and then uses one more parameter to determine the slope on an original scale of p/t versus $E \mu_f/\mu_t$, where the μ are the photoelectric and total linear attenuation coefficients of Ge. The more widely accepted approach where the p/t ratio is a linear function on a log-log scale of the photon energy could also be restricted to one degree of freedom by setting the (160 keV, 1) data point, however, from practical experience this appears to be too high a value, and instead the (90 keV, 1) data point was taken. In the implementation, the user can use one or more sources for the p/t calibration, all of them necessarily being single photon emitters (meaning that ^{65}Zn and ^{57}Co are not allowed). If the user employs more than one, the (90 keV, 1) data point is not used.

For the full-energy peak efficiency curve determination, he can use any mixture of radionuclides with known, preferably traceable activity and emitting a suitable range of gamma-ray energies. After fitting the curve to the points, the efficiencies are converted from the actual calibration counting geometry to point-source geometry and stored. If the source is small as compared to the distance to the detector crystal, this procedure yields accurate results.

An estimate for the escape peak ratio efficiency curves applicable to 20% relative efficiency HPGe detectors is used. The user can improve on this estimate by importing data defining these curves.

Irradiation facility characterization – description of activation rate

Originally, the k_0-method was based on the HØGDAHL convention. BLAAUW[8] adapted this convention and removed all references to the cadmium cut-off energy from the k_0 formulas. In this adapted HØGDAHL convention the capture probability per atom per unit time p is treated as the sum of the integral of the Maxwell-Boltzmann spectrum times the $1/v$ part of the cross section, plus the integral over the epithermal spectrum times the resonances, as expressed in Eq. (1):

$$p = \Phi_t \sigma_0 + \Phi_e I_0'(\alpha) = \Phi_t \left(\sigma_0 + I_0'(\alpha)/f' \right) \quad (1)$$

where

$$\Phi_t = v_0 n = v_0 \int_0^\infty \Phi \frac{1}{v} \frac{2v^3}{v_0^4} e^{-(v/v_0)^2} \mathrm{d}v \quad (2)$$

This approach is valid only if the capture cross section is indeed $1/v$ in the thermal region, say below 0.65 eV. If not, the so-called WESTCOTT g-factor is to be applied to the thermal cross section. This factor is a function of the temperature T of the neutron velocity distribution, and can very easily be used in the adapted convention as shown in Eq. (3):

$$p = \Phi_t g(T)\sigma_0 + \Phi_e I_0'(\alpha) \quad (3)$$

The $g(T)$ factor is defined by:

$$g(T) = \frac{1}{\Phi_t \sigma_0} \int_0^\infty \sigma(v) \Phi \frac{2v^3}{v_T^4} e^{-(v/v_T)^2} \mathrm{d}v \quad (4)$$

and $\sigma(v)$ in turn can be calculated with the Breit-Wigner expression and the known resonance parameters. However, the fact that the velocity distribution of the absorbing nuclei must also be taken into account, a double integration makes the integrals to be evaluated rather time consuming to compute when fitting a T to observed capture rates. So it was decided to enter $g(T)$ values directly in the catalogue of nuclear data, taken from Reference 9. The program interpolates between the tabulated values.

Threshold reactions [(n,p), (n,2n), (n,α), ...] are taken into account as well by assuming that the uranium fission spectrum is applicable to all k_0 irradiation facilities and additionally stating:

$$p = \Phi_t g(T)\sigma_0 + \Phi_e I_0'(\alpha) + \Phi_{fast}\sigma_f \quad (5)$$

where values for σ_f were used as determined at IRI. Summarizing, the activation rate is characterized with five parameters for each target nuclide (σ_0, I_0', E_r, $g(T)$ and σ_f) and five for the neutron spectrum (Φ_t, f, α, T and Φ_{fast}). The spectrum parameters are determined by irradiating and measuring a sample of known composition. In the interpretation, the theoretical activation rates are fitted to the observed activation rates by linear-squares adjustment of all flux parameters Φ_t, f', α, T and Φ_{fast} if possible and if the user so requires. The results can be stored for future use. Alternatively, only Φ_t is adjusted. Any suitable mixture of elements can be used, and the program does not impose any particular procedure.

A good procedure for sample analysis is the stacking of samples and flux monitors alternately in an irradiation container. The program will use all flux monitors in such a stack to find the parameters applicable to a particular sample by fitting a straight line, or if necessary a hyperbola, to the observed parameter values as a function of position in the irradiation container.

Interpretation of sample spectra

Any number of sample spectra obtained after any number of irradiations can be interpreted simultaneously with the program since it uses the holistic interpretation method.[10] In this method, the peak area that would have been obtained if the sample had consisted entirely of an element is calculated. To this end, Eq. (5) is used with the standard formulas for activation and measurement.[11] Cases of complex activation and decay are dealt with as described in Reference 11.

The efficiency curve is used that is the closest match to the sample counting geometry, and it is converted to the sample geometry with a Monte Carlo based effective solid angle approach. Peak areas are calculated for all peaks from all radionuclides detected. However, peaks originating in (n,γ) reactions and characterized by k_0-values were given a weight 400 times larger in the treatment of the system of linear equations than non-k_0 peaks. This also allows for inaccuracy of the IRI cross sections for threshold reactions.

The simultaneous interpretation of spectra results in the automatic resolution of many interferences. For example, ^{140}La is produced both through uranium fission, by way of ^{140}Ba, and directly from ^{139}La (n,γ) reaction. This interference is resolvable through the fact that the apparent half-life of ^{140}La is not the same when obtained through the two different activation routes. The k_0-IAEA program considers this fact as an integral part of its standard interpretation approach.

It is obvious that in fact, the k_0-IAEA program implements absolute standardization. Since, however, all nuclear data used were consistent with the k_0-values for all peaks defined in the k_0-method, and the "k_0-peaks" were given more weight by far, the results are consistent with the k_0-method. The advantage of this approach is that also threshold reactions, fission reactions, interferences with non-k_0 peaks, sum peaks, escape peaks and X-rays could be dealt with in a straightforward manner. The user, in general, does not need to select the peaks for spectrum interpretation. It is, however, possible to deselect peaks that are not properly "understood" by the software, such as the 511 keV and the lead X-rays in case of a lead-shielded detector.

General remarks

Raw spectrum input, as well as peak area input, is possible with commonly used file formats. The user interface is easy to understand and self-explanatory. An extensive help file further assists the user in all relevant problems during installation and application of the program.

The program will interpret all samples and comparators belonging to a single analysis run in batch mode if so desired.

At the reporting stage, the user is offered a vast array of options to customize the output of the program as text files. For example, he can select the coverage factor, the units for concentration, absolute are relative uncertainties, and elements sorted on atomic number or on name.

Experimental

A sample of 221 mg of NIST 2711 Montana Soil in a high-density polyethylene (HDPE) capsule was packaged with a 70 mg zinc foil flux monitor, also in a HDPE capsule, inside a HDPE irradiation container. It was irradiated during 10 seconds in the SBP facility of the Hoger Onderwijs Reactor in Delft ($\Phi_t \approx 1.4 \cdot 10^{17}$ m$^{-2} \cdot$s$^{-1} \pm 1\%$, $f = 28 \pm 1$, $\alpha = 0.09 \pm 0.01$, $\Phi_f/\Phi_t = 0.134 \pm 0.001$, $T = 320 \pm 5$ K). After 15 minutes decay times, it was counted during 5 minutes at a distance of 5 cm of the end cap of a 20% relative efficiency HPGe detector. The flux monitor was counted immediately afterwards during 2 minutes in the same geometry.

The same sample was inserted in a series of eleven similar ones, all consisting of NIST 2711 Montana Soil, stacked alternatingly with pipetted 2 mg zinc flux monitors in the irradiation container, and was irradiated during two hours in the BP3 facility ($\Phi_t \approx 5 \cdot 10^{16}$ m$^{-2} \cdot$s^{-1},

$f = 61 \pm 1$, $\alpha = 0.05 \pm 0.01$, $\Phi_f/\Phi_t = 0.142 \pm 0.001$, $T = 310 \pm 5$ K). After six days decay time, it was counted at 5 cm distance from the end cap of another 20% HPGe detector during 1 hour, and after three weeks in a well-type detector during 1 hour, same as the other samples and flux monitors in the series.

The neutron spectrum parameters as well as the detector efficiency curves of the irradiation facilities had been determined previously, with Au, Zr, and Fe flux monitors. All that information was imported in the k_0-IAEA program.

The peaks in the spectra were fitted with the in-house IRI software and then exported to the formats needed by the k_0-IAEA program.

For the SBP irradiation, the Φ_t observed with the co-irradiated flux monitor was used for the sample interpretation. The BP3 flux monitors were interpreted in terms of Φ_t and a parabolic curve was fitted to the monitors near the sample of interest by the program, in order to derive the best estimate for the Φ_t of the sample. Then, the spectra of the sample were interpreted simultaneously. Only the lead X-rays and the 511 keV peak were explicitly disregarded during the interpretation. Deselecting a few more might have improved the results, but we intended to demonstrate the power of the program by not doing that.

Results

In Fig. 1, the residuals of the three spectra obtained from the sample are shown, that is, the differences between the measured spectra and the spectra as expected from the calculated concentrations, divided by their own uncertainties. The uncertainties in the measured peak areas are purely those stemming from counting statistics, the uncertainties in the expected peak areas comprise the uncertainties of the k_0-values (or 20% in the absence thereof) as well as the propagated χ_r^2 in case of conflicting linear equations. Such residuals should fall in the range between −3 and 3, 95% of them between −2 and 2. The results obtained mostly satisfy this criterion, indicating that indeed, virtually all peaks are understood properly by the program.
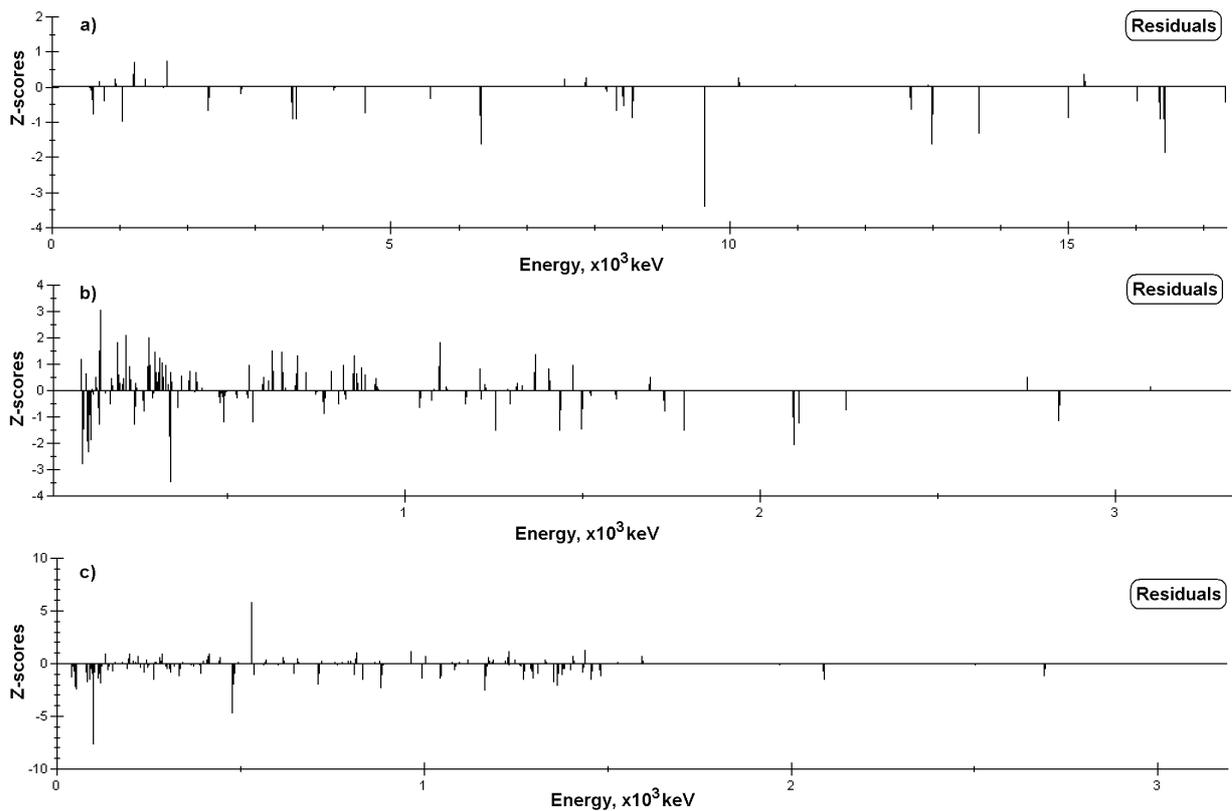

Fig. 1. Residuals of measured and expected spectra of the short-lived irradiation and counting (a), long-lived irradiation and early counting (b), and long-lived and well-type detector counting (c)
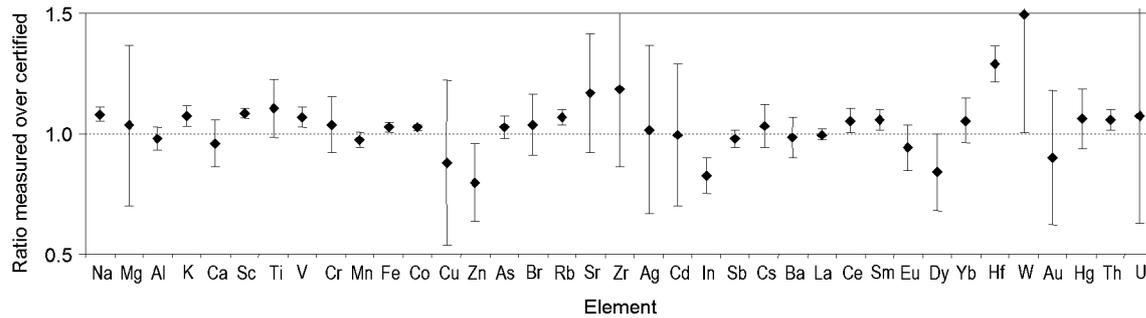
Fig. 2. Ratios of reported to certified concentrations in the NIST 2711 River Sediment sample. The error bars shown exclusively reflect the 1 s.d. uncertainties as reported by the k_0-IAEA program, that is the accuracies of the measured concentrations. Uncertainties in certified concentrations were not taken into consideration at all
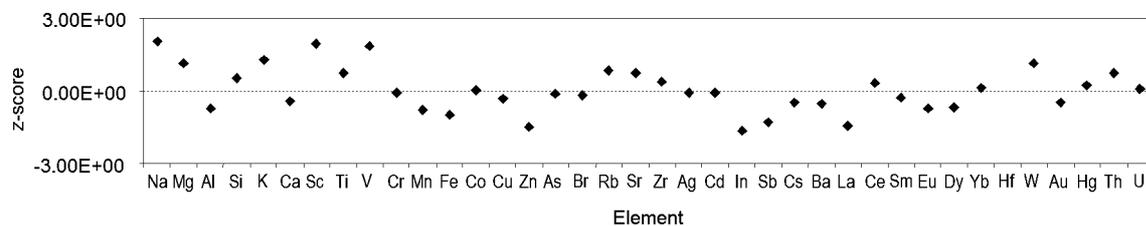

Fig. 3. Residuals of reported to certified concentrations in the NIST 2711 River Sediment sample. The uncertainties used in the calculation were the reported uncertainties by the k_0-IAEA program exclusively, that is the accuracies of the measured concentrations. Uncertainties in certified concentrations were not taken into consideration at all

In Fig. 2, the results are shown in terms of concentrations, as compared to the certified values. The 1 s.d. uncertainties consist of the reported uncertainties of the k_0-IAEA program exclusively. These uncertainties comprise the uncertainties in the sample and flux monitor masses, k_0-values, the peak area statistics, χ_r^2 propagation from the linear-least-squares solution to the linear systems of equations in the holistic approach, as well as the uncertainties in Φ_t, f, and α, where the negative correlation between f and α is taken into account. In the Delft experience of the past 15 years, uncertainties assembled this way serve very well as accuracies, that is as predictors of how far removed from the truth the result might be.

In Fig. 3 the residuals of the comparison with the certificate are shown, again employing only the k_0-IAEA reported uncertainties. The graphs show that the agreement of measured concentrations with the given values is perfect in a statistical sense.

Discussion

The k_0-IAEA program is not a faithful, "vanilla" implementation of the k_0-method. It is much more.

It makes it easier for the user to get started, because detector calibration can be performed in the geometry to be used, and with only two spectra, using commonly available sources. This makes it possible to use well-type detectors, it obviates the fine-tuning process of detector dimension information, and generally improves accuracy because of much smaller correction factors occurring in the conversion from reference geometry efficiency to actual sample geometry efficiency.

Instead of taking only the hundreds of peaks that were associated with k_0-values into account, the program takes all the peaks in the spectra, observed or expected, into account (with the exception of peaks that result from random summing). It is therefore quite robust with respect to interference corrections and reliable in identifying the origins of peaks. This robustness is further enhanced when simultaneously interpreting of spectra from different irradiations and/or measurements.

The user interface offers many graphs, e.g., as shown in Fig. 1, that provide the user with quick insight into the quality of his result. Such residual plots, facilitating the user's judgment, are missing too often from many commercial programs, but are offered in k_0-IAEA throughout.

The program has by now been tested on a variety of samples. Given the fact that the underlying philosophy and approaches can be considered to be the combined

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results of decades of experience and development in Gent, Budapest and Delft, the authors have no doubt that it will prove to perform well in a wide range of applications.

The very nice agreement between the certified concentrations and the reported concentrations presented here is better than could be expected given the fact that reported uncertainties only were used in the comparison. It appears that the uncertainties of the k_0-values, which form the largest contribution after the counting statistics, are overestimated. If these uncertainties had been just right, the uncertainties in the certified concentrations would have to be taken into account to get a result as shown in Fig. 3, and then only in a perfect world.

Conclusions

It has been demonstrated that the new k_0-IAEA software is performing well even under difficult working conditions (well-type detectors). The holistic approach of evaluation of results minimizes the need for user interaction with the routines.

References

1. M. EGUSKIZA, P. ROBOUCH, U. WATJEN, F. DE CORTE, J. Radioanal. Nucl. Chem., 257 (2003) 669.
2. F. DE CORTE, A. SIMONITS, Atomic Data and Nuclear Data Tables, 85 (2003) 47.
3. M. BLAAUW, P. ROBOUCH, B. SMODIS, "The official k_0 website", www.k0naa.org
4. M. BLAAUW, "The k_0-consistent IRI Gamma-ray Catalogue for INAA", Interfaculty Reactor Institute, Delft, The Netherlands, 1996.
5. R. B. FIRESTONE, Table of Isotopes, CD-ROM edition, version 1.0, Wiley Interscience, 1996.
6. P. DE FELICE, P. ANGELINI, A. FAZIO, R. BIAGINI, Appl. Radiation Isotopes, 52 (2000) 745.
7. M. BLAAUW, Nucl. Instr. Meth., A332 (1993) 493.
8. M. BLAAUW, P. BODE, M. DE BRUIN, J. Radioanal. Nucl. Chem., 152 (1991) 435.
9. N. E. HOLDEN, Temperature Dependence of the Westcott g-Factor for Neutron Capture Reactions in ENDF/B-VI, presented at the 36th IUPAC general asembly, Aug 7–15 1991, Germany, BNL-46465.
10. M. BLAAUW, Nucl. Instr. Meth., A (1994) 269.
11. M. BLAAUW, Appl. Radiation Isotopes, 44 (1993) 1225.